

PATENT SPECIFICATION

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(54) BITUMINOUS PRODUCTS CONTAINING POLYURETHANES



(71) We, NAPHTACHIMIE, a body corporate organised and existing under the laws of France, of 203, rue de Faubourg, St. Honore 75, Paris 8e, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention concerns bituminous products having thermoplastic properties and containing polyurethanes.

It is known that certain mechanical characteristics of substances such as coal-tars, which are used for pointing pieces of stonework, may be improved by incorporating substantial amounts of polyurethane, of the order of from 20 to 50% by weight into the substances. A disadvantage of this method is that it results in substances which are not thermoplastic and which consequently cannot be used in a molten state. Also this method cannot be applied to petroleum bitumens owing to the poor compatibility of the latter with quantities of polyurethane of the above order.

It has now been found that by incorporating small amounts of certain polyurethanes into petroleum bitumens bituminous products can be prepared having mechanical properties that are substantially improved with respect to those of the starting bitumens. It has also been found that these bituminous products have thermoplastic properties and can therefore be prepared in a workshop and subsequently used on a site in a manner similar to that in which the bitumens from which they are derived are used.

Accordingly, the present invention provides a thermoplastic bituminous product comprising a petroleum bitumen and a quantity of polyurethane not exceeding 5% by weight, the polyurethane being made from a polyhydroxy compound containing more than four hydroxy groups in the molecule or two or more polyhydroxy compounds of which at least one contains more than four hydroxy

groups in the molecule and an organic polyisocyanate.

In accordance with the present invention, such bituminous products are prepared by incorporating a polyhydroxy compound containing more than four hydroxy groups in the molecule and an organic polyisocyanate into a previously fluidized petroleum bitumen, a polyurethane subsequently being formed in the bitumen by polymerisation of the polyhydroxy compound with the organic polyisocyanate.

The polyhydroxy compound may be, for example, a polyether-polyol or a polyester-polyol.

The polyhydroxy compound preferably comprises one or more polyetherpolyols containing from 5 to 8 hydroxy groups per molecule and having a mean molecular weight of from 400 to 10,000. These polyether-polyols can be prepared by condensing one or more widely varying multi-functional starting materials such as sorbitol and sucrose, with an alkylene oxide such as ethylene oxide of propylene oxide or simultaneously or sequentially with two or more of these alkylene oxides.

The organic polyisocyanate is preferably an aromatic polyisocyanate such as toluene-diisocyanate, which is also known as T.D.I., diphenylmethane - diisocyanate which is also known as M.D.I. or polymethylene-polyphenylisocyanate which is also known as P.A.P.I.

The polyisocyanate can also be used in the form of an isocyanate-terminated polyurethane pre-polymer prepared from a polyisocyanate as mentioned above and a polyhydroxy compound, the relative proportions of the polyisocyanate and polyhydroxy compound used being such that the number of isocyanate groups is greater than the number of hydroxy groups, so that isocyanate groups remain free and can subsequently be reacted with other groups containing a labile hydrogen, such as further hydroxy groups.

The bitumen may be any bitumen that is in current use. It may be pure or in the form

[Price 25p]

of a mixture. Examples of suitable bitumens are direct distillation bitumens and oxidised bitumens. If a bitumen containing water is used, the polyisocyanate may be cross-linked at least partially by the water. However, it is preferable to prevent this cross-linking by using a substantially anhydrous bitumen.

The polyhydroxy compound and polyisocyanate may be incorporated into the bitumen in one of several different ways. For example they may both be introduced simultaneously, preferably with agitation after the bitumen has been liquefied by heating or by fluxation. The resulting bituminous product may then be simply re-heated before it is used or alternatively the incorporation could be carried out on a site just before the product is to be used.

It is also possible to carry out the incorporation in two steps. In this case an intermediate product may first be prepared by introducing the polyhydroxy compound and isocyanate into the bitumen separately. For example, the polyhydroxy compound may be introduced after the bitumen has been liquefied by heating or by fluxation and the intermediate product may then be stored. At a later state this intermediate product may be liquefied and the polyisocyanate added. This second step can be carried out either in a workshop or just before use on a site.

Alternatively before the polyhydroxy compound and the organic polyisocyanate are incorporated into the bitumen, all of the organic polyisocyanate is reacted with a portion of the polyhydroxy compound to produce a pre-polymer, the pre-polymer subsequently being incorporated into the bitumen before the remainder of the polyhydroxy compound. The intermediate bituminous product thus obtained can also be stored. At a later stage this intermediate product may be liquefied and additional polyhydroxy compound, and, if desired, additional polyisocyanate may then be incorporated either in a workshop or just before use on a site.

Generally, the total quantities of polyhydroxy compound and organic polyisocyanate used in the preparation of the bituminous product are such that the ratio of the total number of isocyanate groups in the polyisocyanate to the total number of hydroxyl groups in the polyhydroxy compound, is from 1:1 to 2:1. Preferably this ratio is approximately 1.1:1.

The total quantity of polyurethane incorporated into the bituminous product is adjusted according to the mechanical properties desired in the product, from 0.5 to 4% by weight being sufficient in most cases.

Various fillers, particularly chalk, silica, dolomite, talc and kaolin, and polyurethane cross-linking catalysts such as dibutyl tin laurate, can also be introduced into the bitu-

minous product at one or more stages during its preparation.

Products are obtained after incorporation into the fluidized bitumen of all the ingredients that are fluid and consequently easy to apply. After cooling, products according to the invention are in the form of thermoplastic materials of which the general mechanical properties are considerably improved with respect to those of the bitumen used as starting material. Rupture strength is usually increased from 10 to 20 times, elongation to rupture is higher, flow temperatures are very substantially increased, shearing rates are greatly reduced, and brittleness in a cold state is markedly lower.

Products according to the invention are capable of widely varying uses, particularly as coverings. They can also be used for coating, impregnation and/or encasing. Thus for example they can be used for road surfaces. In this case the products are applied either directly or in the form of embedded materials. These products can also be used to seal works of art and buildings, particularly in the form of sealing compounds of the impregnated glass fabric and/or felt types.

The following Example illustrates the invention.

Example

Into 95 parts by weight of a 115/15 expanded bitumen, heated to a temperature of from 180 to 200°C, there are introduced with agitation 1.9 parts by weight of a polyether-hexol, having a molecular weight of approximately 800 and prepared by the condensation of propylene oxide on sorbitol, and, subsequently, 3.1 parts by weight of a stable pre-polymer prepared from P.A.P.I. and a polypropylene-glycol having a mean molecular weight of approximately 2000, the percentage by weight of the free NCO groups in the pre-polymer being approximately 19%.

Test pieces are immediately cast from the resulting product, which contains a total of 5% by weight of polyurethane, and after solidification, they are used to determine the rupture strength and flow capacity of the products as described below.

The rupture strength of the product is measured on dumbbell-shaped test pieces in accordance with the norm NFT 46 002. It is found to be 10 bars, whereas the rupture strength of the starting bitumen is 0.5 bar, under the same conditions. The test pieces can be elongated by 30%, instead of only a few percent as is the case with the starting bitumen, before rupture occurs.

The flow capacity of the product at 80°C is measured on a cylindrical test piece having a length of 10 cm and a diameter of 2 cm. This test piece is placed in a polyvinyl chloride sheath which is arranged vertically in an oven at 80°C. The height of the meniscus is

measured after 24 hours and found to be 2 to 3 mm. The flow capacities of the starting 115/15 bitumen and of three bituminous products prepared in a manner similar to that described above, but respectively containing only 1, 2 and 3% by weight of polyurethane are determined in a similar manner. It is found that the starting 115/15 bitumen drains off entirely in 2 hours, the product containing 1% of polyurethane flows away entirely in 24 hours, the product containing 2% of polyurethane gives a meniscus of about 1 cm after 24 hours and the product containing 3% gives a meniscus of 3—5 mm after 24 hours.

WHAT WE CLAIM IS:—

1. A thermoplastic bituminous product comprising a petroleum bitumen and a quantity of polyurethane not exceeding 5% by weight, the polyurethane being made from a polyhydroxy compound containing more than four hydroxy groups in the molecule or two or more polyhydroxy compounds of which at least one contains more than four hydroxy groups in the molecule and an organic polyisocyanate.
2. A bituminous product as claimed in Claim 1, in which the quantity of polyurethane is from 0.5 to 4% by weight.
3. A bituminous product as claimed in Claim 1 or 2, also comprising a filler and/or a polyurethane cross-linking catalyst.
4. A method for preparing a thermoplastic bituminous compound as claimed in Claim 1, comprising incorporating a polyhydroxy compound containing more than four hydroxy groups in the molecule or two or more polyhydroxy compounds of which at least one contains more than four hydroxy groups in the molecule and an organic polyisocyanate into a previously fluidized petroleum bitumen, a polyurethane subsequently being formed in the bitumen by polymerisation of the polyhydroxy compound or compounds with the organic polyisocyanate.
5. A method as claimed in Claim 4, in which the polyhydroxy compound contains from 5 to 8 hydroxy groups per molecule and has a mean molecular weight of from 400 to 10,000.
6. A method as claimed in Claim 4 or 5, in which the ratio of the total number of isocyanate groups present in the organic isocyanate to the total number of hydroxy groups

present in the polyhydroxy compound is from 1:1 to 2:1.

7. A method as claimed in Claim 6, in which the said ratio is approximately 1.1:1.

8. A method as claimed in any one of Claims 4 to 7, in which, before the polyhydroxy compound or compounds and the organic polyisocyanate are incorporated into the bitumen, all of the organic polyisocyanate is reacted with a portion of the polyhydroxy compound to produce a pre-polymer, the pre-polymer subsequently being incorporated into the bitumen before the remainder of the polyhydroxy compound.

9. A method as claimed in any one of claims 4 to 7, in which the polyhydroxy compound and the organic polyisocyanate are incorporated in the bitumen simultaneously.

10. A method as claimed in any one of claims 4 to 7, in which the polyhydroxy compound and the organic polyisocyanate are incorporated in the bitumen separately.

11. A method as claimed in any one of claims 4 to 10, in which the bitumen is substantially anhydrous.

12. A method as claimed in any one of claims 4 to 11, in which a filler and/or a polyurethane cross-linking catalyst is also incorporated in the bitumen.

13. A method as claimed in claim 4, substantially as hereinbefore described in the foregoing Example.

14. A thermoplastic bituminous product, when prepared by a method as claimed in any one of claims 4 to 13.

15. A method comprising coating, covering, impregnating or encasing an article with, or preparing a road surface or textile-based sealing material from, a product as claimed in any one of claims 1 to 3 and 14.

16. Articles when coated, covered, impregnated or encased with a product as claimed in any one of claims 1 to 3 and 14.

17. Road surfaces comprising a product as claimed in any one of claims 1 to 3 and 14.

18. Sealing materials comprising a textile impregnated with a product as claimed in any one of claims 1 to 3 and 14.

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